Supplementary Material

Drugs of abuse and their metabolites in river sediments: analysis, occurrence in four Spanish river basins and environmental risk assessment

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Table S1. CAS number, main physical-chemical properties, and predicted no-effect concentration (PNEC) of the target analytes in water and sediments.

Compound	CAS number	Molecular formula	Molecular weight	Log K_{ow} [a]	Log K_{oc} [a]	$PNEC_{water}$ (µg/L) [b]	$PNEC_{sed}$ (ng/g) [b]
Cocaine (COC)	50-36-2	$C_{17}H_{21}NO_4$	303.35	2.30	3.28	2.28 [c]	3.65 [c]
Benzoylecgonine (BE)	519-09-5	$C_{16}H_{19}NO_4$	289.33	-1.32 [*]	2.55	2.33	3.73
Cocaethylene (CE)	529-38-4	$C_{18}H_{23}NO_4$	317.38	2.66 [*]	3.54	1.55	2.48
Amphetamine (AM)	300-62-9	$C_9H_{13}N$	135.21	1.76	3.05	24.80	39.66
Methamphetamine (MA)	537-46-2	$C_{10}H_{15}N$	149.23	2.07	3.21	9.74	15.57
3,4-methylenedioxymethamphetamine (MDMA)	537-46-2	$C_{11}H_{15}NO_2$	193.24	2.28	2.70	47.60	76.11
Ephedrine (EPH)	299-42-3	$C_{10}H_{15}NO$	165.23	1.13	1.92	69.90	111.77
Morphine (MOR)	57-27-2	$C_{17}H_{19}NO_3$	285.34	0.89	3.47	5.38	8.60
6-acetylmorphine (6ACM)	2784-73-8	$C_{19}H_{21}NO_4$	327.37	1.55	4.42	3.33	5.32
Heroin (HER)	561-27-3	$C_{21}H_{23}NO_5$	369.41	1.58	3.86	0.53	0.85
Methadone (METH)	76-99-3	$C_{21}H_{27}NO$	309.45	3.93	4.86	0.84	1.34
2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP)	30223-73-5	$C_{20}H_{23}N$	277.40	4.94 [*]	5.67	0.14	0.22
Lysergic acid diethylamide (LSD)	50-37-3	$C_{20}H_{25}N_3O$	323.43	2.95	5.38	0.39	0.62
2-oxo-3-hydroxy-LSD (OH-LSD)	111295-09-1	$C_{20}H_{25}N_3O_3$	355.43	0.39 [*]	2.68	-	-
Δ^9-tetrahydrocannabinol (THC)	1972-08-3	$C_{21}H_{30}O_2$	314.46	6.97	5.79	0.07	0.12
11-hydroxy-Δ^9-tetrahydrocannabinol (OH-THC)	36557-05-8	$C_{21}H_{30}O_3$	330.46	5.33	4.55	0.28	0.45
Cannabidiol (CBD)	74219-29-7	$C_{21}H_{30}O_2$	314.46	8.01 [*]	6.44	0.17	0.27
Cannabinol (CBN)	521-35-7	$C_{21}H_{26}O_2$	310.43	7.23 [*]	5.79	0.08	0.13
Alprazolam (ALP)	28981-97-7	$C_{17}H_{13}ClN_4$	308.77	2.12	6.33	0.08	0.12
Diazepam (DIA)	439-14-5	$C_{16}H_{13}ClN_2O$	284.74	2.82	4.05	0.29	0.46

[a] Data were obtained from the ChemSpider database. Predicted data were generated using the US Environmental Protection Agency`s EPISuite™ ([*] Estimated)

[b] Data were obtained from NORMAN Ecotoxicology DataBase

[c] $PNEC_{water}$ obtained from Mendoza et al. (2014) and $PNEC_{sed}$ by applying the following equation: $PNEC_{sed} = PNEC_{water} * 2.6 * (0.615 + 0.019 * K_{oc})$

Table S2. Total organic carbon (TOC, % C) content of the sediment samples collected during the 2011 sampling campaign.

	Main River	TOC (% C)	Tributary River	TOC (% C)	Tributary River	TOC (% C)
Llobregat basin	LLO1	1.33	CAR1	2.1		
	LLO2	2.24	CAR2	2.81		
	LLO3	1.25	CAR3	1.31		
	LLO4	2.03	CAR4	1.82		
	LLO5	0.56	ANO1	1.06		
	LLO6	0.65	ANO2	4.79		
	LLO7	2.14	ANO3	1.23		
Ebro basin	EBRO1	2.78	OCA	1.98	ESE	0.34
	EBRO2	2.58	ZAD	5.22	CIN1	0.84
	EBRO3	3.95	NAJ	2.85	CIN2	1.83
	EBRO4	1.35	ARG	1.14	RS	2.98
	EBRO5	2.27	GAL1	0.42	SEG	4.86
	EBRO6	3.77	GAL2	2.53	MAT	2.42
	EBRO7	3.05	HUE	1.23	ALG	0.56
	EBRO9	0.71	MAR	2.82		
Jucar basin	JUC1	1.20	CAB1	3.83		
	JUC2	0.65	CAB2	1.89		
	JUC3	1.99	CAB3	1.41		
	JUC4	0.96	CAB4	1.95		
	JUC5	3.43	CAB5	0.85		
	JUC6	0.51	MAG1	2.94		
	JUC7	2.43	MAG2	1.92		
	JUC8	2.55				
Guadalquivir basin	GUA1	0.79	BOR	2.19	GUA-A	1.07
	GUA2	0.68	GUA-M	0.63	GUA-R	1.87
	GUA3	0.69	MAG	0.77		
	GUA4	1.20	GUA-N	0.63		
	GUA5	0.98	YEG	3.43		
	GUA6	0.67	GUA-L	0.84		
	GUA7	0.39	PIC	0.50		
	GUA8	1.14	BEM	0.41		
	GUA9	0.88	CAC	1.00		
			GEN1	0.68		
			GEN2	1.52		
			COR	0.59		
			HER	1.07		

Table S3a. Predicted median concentration (ng/g d.w.) in 2010 and 2011 obtained with the Quantile Regression Models (Median Regression Models) in the Ebro and the Llobregat River basins. Difference between 2011 and 2010 predicted medians and its 95% confidence interval.

Compounds	Year	Ebro basin				Llobregat basin			
		Predicted median conc. (ng/g d.w.)	95%Ci[a]	Δ median (ng/g d.w.)	95%Ci[a]	Predicted median conc. (ng/g d.w.)	95%Ci[a]	Δ median (ng/g d.w.)	95%Ci[a]
Cocaine	2010	0.3	(0.19;0.42)	**(-0.25*)**	(-0.41;0.09)	0.22	(0.09;0.36)	(-0.01)	(-0.20;0.19)
	2011	0.05	(-0.54;0.16)			0.22	(0.08;0.35)		
MDMA	2010	0.08	(0.03;0.13)	(-0.06)		0.03	(-0.03;0.09)	(-0.02)	
	2011	0.02	(-0.03;0.06)			0.01	(-0.04;0.07)		
METH	2010	0.06	(0.00;0.12)	0		0.11	(0.04;0.17)	(-0.05)	(-0.14;0.49)
	2011	0.06	(0.01;0.11)			0.06	(-0.01;0.13)		
EDDP	2010	0.03	(-0.13;0.18)	0.06	(-0.15;0.28)	0.15	(-0.04;0.33)	0.06	(-0.20;0.32)
	2011	0.09	(-0.05;0.23)			0.21	(0.26;0.39)		
Sum	2010	0.41	(-0.03;0.85)	(-0.10)	(-0.70;0.50)	0.32	(-0.19;0.83)	0.27	(-0.46;1.00)
	2011	0.31	(-0.09;0.71)			0.59	(0.08;1.10)		
Sum No Cannabinoids	2010	0.39	(0.03;0.76)	(-0.08)	(-0.58;0.42)	0.32	(-0.11;0.74)	0.27	(-0.34;0.88)
	2011	0.31	(-0.02;0.64)			0.59	(0.16;1.01)		

*Statistically significant difference between predicted median in 2011 and 2010 concentrations (p-value ≤ 0.05)

[a] 95% Confidence Interval

Table S3b. Predicted median concentration (ng/g d.w.) in 2010 and 2011 obtained with the Quantile Regression Models (Median Regression Models) in the Jucar and the Guadalquivir River basins. Difference between 2011 and 2010 predicted medians and its 95% confidence interval.

Compounds	Year	**Jucar basin**				**Guadalquivir basin**			
		Predicted median conc. (ng/g d.w.)	95%Ci[a]	Δ median (ng/g d.w.)	95%Cia	Predicted median conc. (ng/g d.w.)	95%Ci[a]	Δ median (ng/g d.w.)	95%Ci[a]
Cocaine	2010	0.24	(0.11;0.37)	(-0.13)	(-0.32;0.05)	0.31	(0.20;0.41)	**(0.32*)**	(0.17;0.47)
	2011	0.11	(-0.03;0.24)			0.63	(0.52;0.74)		
MDMA	2010	0.01	(-0.04;0.07)	0		0.01	(-0.03;0.06)	0	
	2011	0.01	(-0.04;0.07)			0.01	(-0.03;0.06)		
METH	2010	0.20	(0.13;0.26)	**(-0.14*)**	(-0.23;-0.04)	0.20	(0.15;0.25)	**(-0.14*)**	(-0.21;0.06)
	2011	0.06	(-0.01;0.13)			0.06	(0.01;0.11)		
EDDP	2010	0.03	(-0.15;0.20)	0		0.03	(-0.12;0.17)	0	
	2011	0.03	(-0.15;0.20)			0.03	(-0.12;0.17)		
Sum	2010	1.01	(0.46;1.56)	(-0.49)	(-1.23;0.26)	0.56	(0.16;0.95)	0.13	(-0.44;0.69)
	2011	0.53	(0.03;1.02)			0.68	(0.28;1.08)		
Sum No Cannabinoids	2010	0.47	(0.06;0.89)	0.05	(-0.54;0.64)	0.56	(0.23;0.88)	0.13	(-0.34;0.59)
	2011	0.53	(0.11;0.94)			0.68	(0.35;1.01)		

*Statistically significant difference between predicted median in 2011 and 2010 concentrations (p-value ≤ 0.05)

[a] 95% Confidence Interval

Table S4. Concentrations of cocaine, MDMA, diazepam, methadone, and EDDP in the sampling stations where they were positively identified in both the water and sediment compartments and experimental K_D obtained.

			Cocaine (n=65)			**MDMA (n=11)**			**Diazepam (n=6)**			**Methadone (n=58)**			**EDDP (n=34)**		
			Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)
Llobregat basin	2010	LLO3	24	171	7.2												
		LLO4	6.8	252	37							1.7	164	96			
		LLO5	4.2	223	53												
		LLO7	5.6	353	63				26	249	9.7	3.8	472	126	13	1180	94
		CAR1										0.57	276	483			
		CAR2	0.89	380	426							0.46	194	422			
		CAR4	0.81	374	461							2.3	510	221	8.0	1235	154
		ANO1	2.8	170	60												
		ANO2	1.6	474	298	7.6	133	18				9.6	1100	114	14	3835	276
		ANO3	9.8	170	17												
	2011	LLO4										1.1	191	176	3.1	680	219
		LLO5	2.2	244	110												
		LLO6	2.7	216	80												
		LLO7	3.6	540	151				13	1320	99	15	945	65	34	3715	109
		CAR3													1.8	635	359
		CAR4	1.9	330	178	4.3	174	40				3.1	885	286	7.9	3345	422
		ANO1	1.2	403	342												
		ANO2	7.1	498	70	46	830	18	7.6	274	36	20	5700	285	50	15800	319
		ANO3				12	93	8				5.6	333	59	17	2535	148
Ebro basin	2010	EBRO4	14	310	22												
		EBRO6	3.5	975	280							0.92	1260	1370	3.4	4260	1249
		EBRO9	0.73	333	455												

Table S4. (continued)

			Cocaine (n=65)			MDMA (n=11)			Diazepam (n=6)			Methadone (n=58)			EDDP (n=34)		
			Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)
	2010	ZAD				2.7	306	113	3.1	243		11	3740	346	45	9450	211
		NAJ	2.5	173	70							0.67	162	241			
		ARG				3.1	245	78				4.9	1370	281	14	2760	200
		HUE	34	1040	30	3.0	87	29				2.0	700	345	9.9	5850	593
		MAR	2.8	321	114	0.84	76	90									
		CIN1										2.0	391	193			
		RS	3.4	276	80												
	2011	EBRO2	1.1	281	260	0.27	111	419									
Ebro basin		EBRO3										0.37	338	915	0.62	1375	2236
		EBRO4	1.3	405	307							0.59	171	291			
		EBRO5	3.5	391	113												
		EBRO6	4.6	243	52							0.89	685	771	1.3	2460	1937
		EBRO7	9.7	166	17							2.9	1666	57	0.47	795	1688
		ZAD	6.7	437	65	5.1	432	84				4.8	2685	561	14	7800	542
		ARG										5.0	945	188	13	2430	188
		GAL2										1.0	302	299	1.6	865	554
		HUE	25	444	17	14	188	13				4.5	650	145	14	6800	482
		SEG	1.9	363	196							1.7	1305	759	6.0	3615	599
	2010	JUC1										2.4	197	81			
Jucar basin		JUC2	2.2	276	125							1.8	198	110	1.4	491	343
		JUC3	2.8	381	137							2.2	925	420	5.8	755	131
		JUC5	1.9	227	117							0.77	174	224			
		JUC6	2.5	234	92							1.2	167	136			

Table S4. (continued)

			Cocaine (n=65)			MDMA (n=11)			Diazepam (n=6)			Methadone (n=58)			EDDP (n=34)		
			Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)
Jucar basin	2010	JUC7	3.4	225								1.1	289	255			
		JUC8	8.1	316								1.2	298	244	2.6	605	237
		CAB1										1.0	277	279			
		CAB2	1.8	268								0.41	207	499			
		MAG1	3.4	307					1.9	197		2.1	1075	524	4.8	675	140
	2011	JUC3	3.8	287								1.3	486	379	6.3	1915	306
		JUC6	2.4	525													
		JUC8	1.8	525											2.2	905	404
		CAB1	2.9	4560													
		CAB2	0.54	595													
		CAB4	2.4	346													
		MAG1							2.3	131		1.2	555	474	2.7	645	237
		MAG2	1.5	399													
Guadalquivir basin	2010	GUA4										0.79	236	300	2.4	625	256
		GUA6	4.6	307								1.0	381	369			
		GUA7										0.45	186	415			
		GUA8										0.42	235	554			
		BOR	1.5	790								0.31	165	532			
		GUA-N	2.3	500								1.1	305	274	2.5	720	286
		YEG										0.24	198	818			
		GUA-L										0.38	251	668			

Table S4. (continued)

			Cocaine (n=65)			MDMA (n=11)			Diazepam (n=6)			Methadone (n=58)			EDDP (n=34)		
			Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)	Water (ng/L)	Sed. (ng/kg d.w.)	K_D (L/kg)
	2010	GEN1	9.9	535								1.4	185	128	4.5	1050	230
		GEN2	2.9	269								0.69	249	359			
		HER										0.43	165	379			
		GUA-A										14	1660	119	34	5800	172
		GUA-R										0.43	193	446			
	2011	GUA1	1.0	630													
		GUA2	3.9	1100													
		GUA4	3.0	4695								2.1	32600	15673			
		GUA5	2.4	2215													
Guadalquivir basin		GUA6	3.7	750													
		GUA7	3.6	4990													
		GUA8	1.3	1020								0.65	620	957			
		GUA9	0.94	680													
		BOR	1.2	600													
		GUA-N	7.0	700								2.8	200	72			
		GUA-L	1.1	510													
		GEN1	15	424								2.9	368	126	5.5	960	175
		COR	0.81	322								0.50	236	468			
		HER	5.5	760								0.98	194	198			
		GUA-A	3.1	1305								13	3910	313	16	9650	603
Average all basins					**281**			**88**			**64**			**619**			**474**

Table S5. Hazard Quotient (HQ) values calculated for each compound at each sampling point during the 2010 sampling campaign.

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
Llobregat basin (main river)	LLO1	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	LLO2	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	LLO3	<0.1	0	0	0	0	0	0	0	0	333	0	98	***333***	***431***
	LLO4	<0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.2*
	LLO5	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	LLO6	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	LLO7	<0.1	0	0	0	0	0	0.5	0.4	5.4	53	0	0	***53***	***60***
Ebro basin (main river	EBRO1	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	EBRO2	<0.1	0	0	<0.1	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	EBRO3	<0.1	0	0	0	0	0	0	<0.1	0.7	0	0	0	*0.7*	*0.9*
	EBRO4	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	EBRO5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	EBRO6	0.3	0	0	0	0	0	0	0.9	19	0	0	0	***19***	***21***
	EBRO7	0.2	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.4*
	EBRO8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	EBRO9	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
Jucar basin (main river)	JUC1	0	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.1*
	JUC2	<0.1	0	0	0	0	0	0	0.1	2.2	0	0	0	***2.2***	***2.5***
	JUC3	0.1	0	0	0	0	0	0	0.7	3.4	0	0	0	***3.4***	***4.2***
	JUC4	0.3	0	0	0	0	0	0	0.1	0	0	0	0	*0.3*	*0.5*
	JUC5	<0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.2*
	JUC6	<0.1	0	0	0	0	0	0	0.1	0	36	0	0	***36***	***36***
	JUC7	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	JUC8	<0.1	0	0	0	0	0	0	0.2	2.8	0	0	0	***2.8***	***3.1***

Table S5. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
Guadalquivir basin (main river)	GUA1	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	GUA2	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	GUA3	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	GUA4	<0.1	0	0	0	0	0	0	0.2	2.8	0	0	0	***2.8***	***3.1***
	GUA5	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
	GUA6	<0.1	0	0	0	0	0	0	0.3	0	0	0	0	*0.3*	*0.4*
	GUA7	0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.2*
	GUA8	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	GUA9	<0.1	0	0	0	0	0	0	0.0	0	0	0	0	*<0.1*	*<0.1*
Llobregat basin (tributaries)	CAR1	0	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.2*
	CAR2	0.1	0	0	0	0	0	0.3	0.1	0	0	0	0	*0.3*	*0.5*
	CAR3	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CAR4	0.1	0	0	<0.1	0	0	0	0.4	5.6	0	0	0	***5.6***	***6.1***
	ANO1	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	ANO2	0.1	0	0	<0.1	0	0	0	0.8	17.4	57	0	0	***57***	***75***
	ANO3	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
Ebro basin (tributaries)	OCA	<0.1	0	<0.1	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	ZAD	0.1	0	0	<0.1	0	0	0.5	2.8	43	324	55	338	***338***	***762***
	NAJ	<0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.2*
	ARG	0.1	0	0	<0.1	0	0	0	1.0	13	0	0	0	***13***	***14***
	GAL1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	GAL2	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	HUE	0.3	0	0	<0.1	0	0	0	0.5	27	55	0	0	***55***	***83***
	MAR	<0.1	0	0	<0.1	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*

Table S5. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
	ESE	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CIN1	0	0	0	0	0	0	0	0.3	0.0	40	0	0	***40***	***40***
	CIN2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	RS	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	SEG	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	MAT	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	ALG	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
Jucar basin (tributaries)	CAB1	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	CAB2	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.2*
	CAB3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	CAB4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	CAB5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	MAG1	<0.1	0	0	0	0	0	0.4	0.8	3.1	0	0	0	***3.1***	***4.4***
	MAG2	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
Guadalquivir basin (tributaries)	BOR	0.2	0	0	0	0	0	0	0.1	0	0	0	0	*0.2*	*0.3*
	GUA-M	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	MAG	<0.1	0	0	0	0	0	0	0.3	0	0	0	0	*0.3*	*0.4*
	GUA-N	0.1	0	0	0	0	0	0	0.2	3.3	0	0	0	***3.3***	***3.6***
	YEG	<0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.2*	*0.2*
	GUA-L	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	PIC	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	BEM	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	CAC	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	GEN1	0.1	0	0	0	0	0	0	0.1	4.8	0	0	0	***4.8***	***5.1***

Table S5. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
	GEN2	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	COR	<0.1	0	0	0	0	0	0	0.3	0	0	0	0	*0.3*	*0.3*
	HER	<0.1	0	0	0	0	0	0	0.1	0.9	0	0	0	*0.9*	***1.1***
	GUA-A	<0.1	0	0	0	0	0	0	1.2	26	0	0	0	***26***	***28***
	GUA-R	<0.1	0	0	0	0	0	0	0.1	0	0	0		*0.1*	*0.2*
HQ (max)		*0.3*	*0*	*0*	*0*	*0*	*0*	*0.5*	***2.8***	***43***	***333***	***55***	***338***		

∑HQ values between 1 and 10 are indicated in bold, and ∑HQ>10 in red. - Sampling stations where sediments could not be collected

Table S6. Hazard Quotients (HQ) values calculated for each compound at each sampling point during the 2011 sampling campaign.

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
Llobregat basin (main river)	LLO1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	LLO2	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	LLO3	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	LLO4	0	0	0	0	0	0	0	0.1	3.1	0	0	0	***3.1***	***3.2***
	LLO5	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	LLO6	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	LLO7	0.1	0.2	<0.1	0	0	0	2.8	0.7	17	127	0	0	***127***	***148***
Ebro basin (main river)	EBRO1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	EBRO2	<0.1	0	0	<0.1	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
	EBRO3	0	0	0	0	0	0	0	0.3	6.3	0	0	0	***6.3***	***6.5***
	EBRO4	0.1	0	0	0	0	0	0	0.1	0	0	0	0	*0.1*	*0.2*
	EBRO5	0.1	0	0	0	<0.1	0	0	0	0	0	0	0	*0.1*	*0.1*
	EBRO6	<0.1	0	0	0	0	0	0	0.5	11	0	0	0	***11***	***12***
	EBRO7	<0.1	0	0	0	0	0	0	0.1	3.6	0	0	0	***3.6***	***3.8***
	EBRO8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	EBRO9	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
Jucar basin (main river)	JUC1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	JUC2	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	JUC3	<0.1	0	0	0	0	0	0	0.4	8.7	0	0	0	***8.7***	***9.1***
	JUC4	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	JUC5	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	JUC6	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	JUC7	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*

Table S6. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
	JUC8	0.1	<0.1	0	0	0	0	0	0	4.1	0	0	0	***4.1***	***4.3***
Guadalquivir basin (main river)	GUA1	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
	GUA2	0.3	0	0	0	<0.1	0	0	0	0	0	0	0	*0.3*	*0.3*
	GUA3	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	GUA4	1.3	0	0	0	<0.1	0	0	24	0	0	0	0	***24***	***26***
	GUA5	0.6	0	0	0	<0.1	0	0	0	0	0	0	0	*0.6*	*0.6*
	GUA6	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
	GUA7	1.4	0	0	0	0	0	0	0	0	0	0	0	***1.4***	***1.4***
	GUA8	0.3	0	0	0	0	0	0	0.5	0	0	0	0	*0.5*	*0.7*
	GUA9	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
Llobregat basin (tributaries)	CAR1	0.0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CAR2	0.0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CAR3	0.0	0	0	0	0	0	0	0	2.9	0	0	0	***2.9***	***2.9***
	CAR4	<0.1	0	0	<0.1	0	0	0	0.7	15	0	0	0	***15***	***16***
	ANO1	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	ANO2	0.1	0	0	<0.1	0	0	0.6	4.3	72	0	0	0	***72***	***77***
	ANO3	0.2	0	0	<0.1	0	0	0	0.2	12	0	0	0	***12***	***12***
Ebro basin (tributaries)	OCA	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	ZAD	0.1	0	<0.1	<0.1	0	0	0	2.0	35	0	0	0	***35***	***38***
	NAJ	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	ARG	0	0	0	0	0	0	0	0.7	11	0	0	0	***11***	***12***
	GAL1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	GAL2	0	0	0	0	0	0	0	0.2	3.9	0	0	0	***3.9***	***4.2***
	HUE	0.1	0	0	<0.1	0	0	0	0.5	31	0	0	0	***31***	***32***

Table S6. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
	MAR	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	ESE	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CIN1	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CIN2	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	RS	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	SEG	<0.1	0	0	0	0	0	0	1.0	16	0	0	0	***16***	***18***
	MAT	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	ALG	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
Jucar basin (tributaries)	CAB1	1.2	0.1	0	0	0	0	0	0	0	0	0	0	***1.2***	***1.4***
	CAB2	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
	CAB3	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	CAB4	<0.1	0	0	0	0	0	0	0.3	0	0	0	0	*0.3*	*0.3*
	CAB5	0	0	0	0	0	0	0	0.0	0	0	0	0	*<0.1*	*<0.1*
	MAG1	0	0	0	0	0	0	0.3	0.4	2.9	0	0	0	***2.9***	***3.6***
	MAG2	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
Guadalquivir basin (tributaries)	BOR	0.2	0	0	0	0	0	0	0	0	0	0	0	*0.2*	*0.2*
	GUA-M	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	MAG	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	GUA-N	0.2	0	0	0	0	0	0	0.1	0	0	0	0	*0.2*	*0.3*
	YEG	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	GUA-L	0.1	0	0	0	0	0	0	0	0	0	0	0	*0.1*	*0.1*
	PIC	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*
	BEM	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	CAC	0	0	0	0	0	0	0	0	0	0	0	0	*0*	*0*

Table S6. (continued)

		COC	BE	EPH	MDMA	MA	ALP	DIA	METH	EDDP	THC	CBD	CBN	*HQ (max)*	*∑HQ*
	GEN1	0.1	0	0	0	0	0	0	0.3	4.4	0	0	0	***4.4***	***4.8***
	GEN2	0.3	0	0	0	0	0	0	0	0	0	0	0	*0.3*	*0.3*
	COR	<0.1	0	0	0	0	0	0	0.2	0	0	0	0	*0.2*	*0.3*
	HER	0.2	0	0	0	0	0	0	0.1	0	0	0	0	*0.2*	*0.4*
	GUA-A	0.4	0	0	0	0	0	0	2.9	44	0	0	0	***44***	***47***
	GUA-R	<0.1	0	0	0	0	0	0	0	0	0	0	0	*<0.1*	*<0.1*
HQ (max)		*1.4*	*0.2*	*0*	*0*	*0*	*0*	*2.8*	***24***	***72***	***127***	*0*	*0*		

∑HQ values between 1 and 10 are indicated in bold, and ∑HQ>10 in red. - Sampling stations where sediments could not be collected